

XP-002251037

Page: 108

117: 50766j Manufacture of perylene-3,4,9,10-tetracarboxylic acid dimide. Okazaki, Hiroshi; Yanai, Hiroshi; Kobayashi, Masaru (Nippon Steel Chemical Co., Ltd.) Jpn. Kokai Tokkyo Koho JP 03,223,282 [91,223,282] (Cl. C07D471/04), 02 Oct 1991; Appl. 90/14,974, 26 Jan 1990; 4 pp. The title compd. (I), useful as an intermediate for vat dyes, is manufd. by condensation of 1,8-naphthalimide with heating in the presence of an alkali metal hydroxide, followed by oxidn. in a high-boiling coal tar- or petroleum-derived oil or an aprotic polar solvent. The condensation and the oxidn. may be carried out simultaneously. Thus, a mixt. of 1,8-naphthalimide 20, 86% aq. KOH 60, and a coal tar-derived methylnaphthalene fraction 120 g was heated 10 h at 230° to give leuco-I, which was dispersed in H<sub>2</sub>O and oxidized with air to give 19.0 g I.

(19) Japanese Patent Office (JP)

(11) Publication number

H3-223282

(12) THE LAID-OPEN PATENT GAZETTE (A)

(43) Publication date 2<sup>nd</sup> October 1991

(51) Int.Cl. <sup>5</sup>	Identification code	Office filing number
C 07 D 471/04	103	8829-4C
Request for examination: Not yet received		
Number of claims: 4		
(Total number of pages [in the Japanese]: 4)		

(54) Title of the invention                      Method for the production of perylene-3,4,9,10-tetracarboxylic acid diimide

(21) Patent application number              H2-14974

(22) Application date                              26<sup>th</sup> January 1990

(72) Inventor                                      Hiroshi OKAZAKI  
11-24-12 Oaza Jiyugaoka Munekata-shi, Fukuoka-ken

(72) Inventor                                      Hiroshi YANAI  
2-13-2-306 Nakai, Kokura Kita-ku, Kitakyushu-shi  
Fukuoka-ken

(72) Inventor                                      Masaru KOBAYASHI  
1-8-24 Nakao, Yawata Higashi-ku, Kitakyushu-shi  
Fukuoka-ken

(71) Applicant                                    Nippon Steel Chemical Co., Ltd.  
5-13-16 Ginza, Chuo-ku, Tokyo-to

(74) Agent                                        Patent attorney Katsuo NARUSE, and 3 others

## Specification

## 1. Title of the invention

Method for the production of perylene-3,4,9,10-tetracarboxylic acid diimide

## 2. Scope of the patent claims

(1) A method for the production of perylene-3,4,9,10-tetracarboxylic acid diimide, characterised in that when perylene-3,4,9,10-tetracarboxylic acid diimide is produced by condensing 1,8-naphthalimide using an alkali metal hydroxide with heating, and then oxidising, the condensation reaction is performed in the presence of a high-boiling solvent.

(2) The method for the production of perylene-3,4,9,10-tetracarboxylic acid diimide according to Claim 1, where the oxidation is performed at the same time as the condensation reaction.

(3) The method for the production of perylene-3,4,9,10-tetracarboxylic acid diimide according to Claim 1, where the high-boiling solvent is an oil separated from coal tar or petroleum.

(4) The method for the production of perylene-3,4,9,10-tetracarboxylic acid diimide according to Claim 1, where the high-boiling solvent is an aprotic polar solvent.

## 3. Detailed description of the invention

Field of industrial use

The present invention relates to a method for the production of perylene-3,4,9,10-tetracarboxylic acid

diimide, which is an important intermediate in the field of dyes, pigments and electronic materials.

#### Prior art

Perylene-3,4,9,10-tetracarboxylic acid diimide has long been known as an important starting material for the production of acenaphthene-based builder dyes, and recently it has received attention as a starting material for the production of optical organic materials. It is produced by coupling (condensing) 1,8-naphthalimide by means of an alkali fusion reaction, then oxidising (BIOS FINAL REPORT Nr. 1487, 21, D.R.P. 762357, 276956; Frdl., 12, 492, 493, Journal of Industrial Chemistry 54, 479 (1951), Japanese Unexamined Patent S59-205,376 G). A method whereby the coupling reaction and the oxidation reaction are performed simultaneously in a single step has also been reported (Bur. Pat. 54,806).

#### Problems to be resolved by the invention

However, with the conventional technology, a special reaction vessel is required because the product formed in the fusion reaction is a very high viscosity slurry, despite the use of a large excess of alkali with respect to the 1,8-naphthalimide, and there are also problems such as the rapid deterioration of the reaction vessel. Moreover, because the reaction product is highly viscous when the condensation reaction product is separated from the alkali melt, high-temperature water must be added to the high concentration alkali solution, and so there are problems regarding safety during production. There is also the problem of treating a large excess of separated alkali as waste solution, and so forth.

As a result of diligent research into resolving the above-mentioned problems, the present inventors discovered that it is possible to produce perylene-3,4,9,10-tetracarboxylic acid diimide by dispersing 1,8-naphthalimide in a high-boiling solvent, performing a condensation reaction using an alkali metal hydroxide, and oxidising. They also discovered that it is possible to recover and reuse the high-boiling solvent and the alkali metal hydroxide.

The aim of the present invention is to provide a method for the economical production of a good yield of perylene-3,4,9,10-carboxylic acid diimide from 1,8-naphthalimide by a highly safe production operation where it is relatively easy to perform the reaction continuously.

#### Means of resolving the problems

Specifically, the present invention is a method for producing perylene 3,4,9,10-tetracarboxylic acid diimide by adding a high-boiling solvent to 1,8-naphthalimide and an alkali metal hydroxide so that the reaction system forms a relatively low viscosity slurry, condensing by heating to a temperature at which condensation can proceed, and oxidising.

The present invention is described in detail below.

There are no particular limitations regarding the high-boiling solvent used in the present invention provided that it is not an acidic material that will hinder the condensation reaction, and that it is in the liquid phase under the reaction conditions, preferably having a boiling point of from 200 to 400°C, although it must be stable with respect to alkali metal hydroxide when heated. The high-boiling solvent is preferably an oil separated from coal tar or petroleum, or an aprotic

polar solvent. Nitrogen-containing aromatic compounds such as quinoline, quinaldine and isoquinoline, which have excellent thermal stability, and tar base oils containing these, are examples of oils separated from coal tar; in addition, methylnaphthalene and fractions containing it also have good thermal stability and are preferred. Kerosene and light oil are examples of oils separated from petroleum, and are particularly good. Obviously, it is also possible to use oils comprising only the compound that is the main structural component of these separated oils. 1,3-dimethyl-2-imidazolidinone, which has good thermal stability with respect to alkali metal hydroxides at high temperature, is preferred as a non-proton donating aprotic high-boiling solvent. It should be noted that these solvents are preferably treated beforehand to remove impurities such as substances that will hinder reaction with phenol or the like, and substances with poor thermal stability. The high-boiling solvent need not dissolve the starting materials such as the alkali metal hydroxide; the whole system should be in the form of a slurry comprising the starting materials dispersed in the high-boiling solvent.

The amount of high-boiling solvent used should be from 2 to 10 times the amount by weight of the 1,8-naphthalimide. If a much greater amount than necessary is used, the reaction time increases, there are more byproducts and the purity of the reaction product decreases. If too little solvent is used, the reaction mixture does not form a slurry and there is an insufficient decrease in viscosity.

The alkali metal hydroxide used in the present invention is preferably potassium hydroxide or sodium hydroxide, and potassium hydroxide is particularly preferred. This

can be used in the form of a solid or an aqueous solution, and the amount of potassium hydroxide used is from 0.5 to 10 parts by weight, preferably from 2 to 5 parts by weight, with respect to the 1,8-naphthalimide. It is preferable to use the alkali metal hydroxide at a concentration of at least 80%, although it is also possible to perform the reaction using an aqueous solution of a concentration of around 50% while distilling off water from the reaction vessel.

The present reaction is performed by heating a mixture of the reaction starting materials as described above, at a temperature of from 180 to 300°C. If the reaction temperature is less than 180°C, the 1,8-naphthalimide conversion rate decreases. The reaction time depends on the amount of high-boiling solvent, the amount of alkali metal hydroxide and the reaction temperature, and is usually from 0.5 to 24 hours.

The condensation reaction product is oxidised to perylene-3,4,9,10-tetracarboxylic acid diimide either after completion of the condensation reaction or at the same time as the condensation reaction. Specifically, after completion of the compensation reaction, solid-liquid separation is performed to isolate the perylene-3,4,9,10-tetracarboxylic acid diimide leuco form, which is then oxidised by a common method such as dispersing in water and bubbling air through, and the oxidation product is obtained by filtration, washed using water and organic solvent or the like, and dried to yield perylene-3,4,9,10-tetracarboxylic acid diimide; or, air-oxidation and separation by filtration are performed as the condensation reaction proceeds, and the product is washed using water and organic solvent, then dried to yield perylene-3,4,9,10-tetracarboxylic acid diimide. If the latter method is adopted, the condensation and

oxidation can be performed in a single step without separating the reaction mixture. In such cases, the oxidation can be performed after completion of the condensation reaction, or at the same time as the condensation reaction. In another method whereby oxidation is performed after completion of the condensation reaction, water is added prior to filtering to form an aqueous solution of alkali metal hydroxide, which is then filtered.

The high-boiling solvent is easily recovered from the filtrate obtained on filtration, and it can be purified by distillation if necessary, then reused. It is also possible to recover the alkali metal hydroxide as an aqueous solution, and in such cases, a highly concentrated aqueous solution can be recovered by regulating the amount of water used during filtration and washing. The recovered aqueous solution of alkali metal hydroxide can be concentrated if necessary and reused. An oxygen-containing gas, preferably air, can be used as the oxidising agent used for the oxidation.

#### Working examples

The present invention is described below by means of working examples. It should be noted that in the working examples, % indicates % by weight.

#### Working example 1

60 g of 86% aqueous potassium hydroxide solution and 20 g of 1,8-naphthalimide were added to 120 g of a methylnaphthalene fraction (44.2%  $\alpha$ -methylnaphthalene, 22.9%  $\beta$ -methylnaphthalene, 26.1% dimethylnaphthalene, 2.3% quinoline, 2.3% acenaphthene, 2.2% fluorene) separated from coal tar, and the system was heated at 230°C and agitated for 10 hours. The temperature was



lowered to 60°C and filtration was performed, and a large amount of water was used for washing to obtain the perylene-3,4,9,10-tetracarboxylic acid diimide leuco form, which was then oxidised by a common method involving dispersion in water and air-oxidation; the oxidation product was subjected to solid-liquid separation, washed using water, washed using methanol, then dried to yield 19.0 g of perylene-3,4,9,10-tetracarboxylic acid diimide.

#### Working example 2

60 g of 86% potassium hydroxide and 20 g of 1,8-naphthalimide were added to 120 g of a methylnaphthalene fraction, and the system was heated at 230°C and agitated for 10 hours. The temperature was lowered to 80°C, then 60 g of water were added, and the system was boiled for 30 minutes, filtered and washed using water to yield the perylene-3,4,9,10-tetracarboxylic acid diimide leuco form. The potassium hydroxide was recovered as an aqueous solution from the filtrate, and the methylnaphthalene fraction was separated and recovered. The leuco form was washed using methanol, then air-oxidised by a common method, and the oxidation product was subjected to solid-liquid separation and washed using water. 18.8 g of perylene-3,4,9,10-tetracarboxylic acid diimide were obtained on drying.

#### Working example 3

60 g of 86% potassium hydroxide and 20 g of 1,8-naphthalimide were added to 120 g of a methylnaphthalene fraction, and the reaction mixture obtained on heating at 220°C was agitated for 10 hours at 220°C while air was blown in at a rate of 140 ml/hour via an air aspiration pipe. The temperature was decreased to 80°C,

then 60 g of water were added, and the system was boiled for 30 minutes, and filtered; the aqueous potassium hydroxide solution and the methylnaphthalene were separated and recovered from the filtrate. The filtered substance was washed using water, washed using methanol, then dried to yield 18.6 g of perylene-3,4,9,10-tetracarboxylic acid diimide.

#### Working example 4

60 g of 86% potassium hydroxide and 20 g of 1,8-naphthalimide were added to 80 g of quinoline, and the reaction mixture was agitated for 12 hours at 210°C. The temperature was decreased to 60°C, then the quinoline was separated and recovered by filtration. The filtered substance was washed using water then washed using methanol to yield the perylene-3,4,9,10-tetracarboxylic acid diimide leuco form. This was then oxidised by a known method to yield 18.3 g of perylene-3,4,9,10-tetracarboxylic acid diimide.

#### Working example 5

60 g of 86% potassium hydroxide and 20 g of 1,8-naphthalimide were added to 80 g of 1,3-dimethyl-2-imidazolidinone, and the system was heated at 225°C and agitated for 6 hours. The system was returned to room temperature then filtered, and the 1,3-dimethyl-2-imidazolidinone was recovered from the filtrate. The filtered substance was washed using a large amount of water to yield the perylene-3,4,9,10-tetracarboxylic acid diimide leuco form. This was then oxidised by a known method to yield 18.8 g of perylene-3,4,9,10-tetracarboxylic acid diimide.

#### Working example 6

120 g of 86% potassium hydroxide and 40 g of 1,8-naphthalimide were added to 320 g of 1,3-dimethyl-2-imidazolidinone, and the system was heated at 225°C and agitated for 6 hours. The temperature was lowered to 170°C, then oxidation was allowed to proceed for 6 hours, with agitation, while air was blown in at a rate of 100 ml/hour via an air aspiration pipe. The system was returned to room temperature, then filtered, and the 1,3-dimethyl-2-imidazolidinone was separated and recovered. The filtered substance was washed using water and dried to yield 37.8 g of perylene-3,4,9,10-tetracarboxylic acid diimide.

#### Working example 7

240 g of 86% potassium hydroxide and 80 g of 1,8-naphthalimide were added to 320 g of 1,3-dimethyl-2-imidazolidinone, and the system was heated at 225°C. The temperature was maintained and the system agitated for 6 hours while air was blown in at a rate of 100 ml/hour. The system was returned to room temperature, then filtered, and the 1,3-dimethyl-2-imidazolidinone was separated and recovered. 240 g of water were added to the filtered substance, and this was boiled for 30 minutes with agitation. Filtration was performed again, the potassium hydroxide was recovered from the filtrate as an aqueous solution, then washing and drying yielded 75.1 g of perylene-3,4,9,10-tetracarboxylic acid diimide.

#### Working example 8

30 g of 86% potassium hydroxide and 10 g of 1,8-naphthalimide were added to 60 g of kerosene and heated at 225°C. The temperature was maintained and air was blown in at 100 ml/hour for 6 hours, with agitation. The

system was returned to room temperature, then filtered, and the kerosene was separated and recovered. 30 g of water were added to the filtered substance, and this was boiled for 30 minutes with agitation. The system was filtered and the potassium hydroxide was recovered from the filtrate as an aqueous solution, and the filtered substance was washed and dried to yield 9.4 g of perylene-3,4,9,10-tetracarboxylic acid diimide.

#### Advantages of the invention

The method of the present invention involves subjecting 1,8-naphthalimide and an alkali metal hydroxide to a condensation reaction in the presence of a high-boiling solvent to economically produce perylene-3,4,9,10-tetracarboxylic acid diimide, which is used as an intermediate in the production of dyes, pigments, electronic materials and the like; moreover, this production method is safe to operate.

Patent applicant      Nippon Steel Chemical Co., Ltd.

Agent                  Patent attorney Katsuo NARUSE (and 3 others)

⑨ 日本国特許庁(JP)

⑩ 特許出願公開

⑫ 公開特許公報(A) 平3-223282

⑮ Int. Cl.<sup>5</sup>  
C 07 D 471/04

識別記号  
1 0 3

庁内整理番号  
8829-4C

⑭ 公開 平成3年(1991)10月2日

審査請求 未請求 請求項の数 4 (全4頁)

⑬ 発明の名称 ベリレン-3, 4, 9, 10-テトラカルボン酸ジイミドの製造方法

⑰ 特 願 平2-14974

⑱ 出 願 平2(1990)1月26日

⑲ 発 明 者	岡 崎 博	福岡県宗像市大字自由ヶ丘11丁目24-12番地
⑲ 発 明 者	箭 内 裕 志	福岡県北九州市小倉北区中井2丁目13-2-306
⑲ 発 明 者	小 林 優	福岡県北九州市八幡東区中尾1丁目8-24
⑲ 出 願 人	新日鐵化学株式会社	東京都中央区銀座5丁目13番16号
⑲ 代 理 人	弁理士 成瀬 勝夫	外3名

明 細 書

1. 発明の名称

ベリレン-3, 4, 9, 10-テトラカルボン酸ジイミドの製造方法。

2. 特許請求の範囲

(1) 1,8-ナフタリイミドをアルカリ金属水酸化物を用いて加熱条件下に縮合反応させ、かつ酸化することによりベリレン-3, 4, 9, 10-テトラカルボン酸ジイミドを製造するに当り、縮合反応を高沸点溶剤の存在下で行うことを特徴とするベリレン-3, 4, 9, 10-テトラカルボン酸ジイミドの製造方法。

(2) 酸化を縮合反応と同時に行う請求項1記載のベリレン-3, 4, 9, 10-テトラカルボン酸ジイミドの製造方法。

(3) 高沸点溶剤がコールタール又は石油から分離される油である請求項1記載のベリレン-3, 4, 9, 10-テトラカルボン酸ジイミドの製造方法。

(4) 高沸点溶剤が非プロトン性極性溶剤である請求項1記載のベリレン-3, 4, 9, 10-テトラカルボン酸ジイミドの製造方法。

3. 発明の詳細な説明

(産業上の利用分野)

本発明は、染料料および電子材料の分野において中間体として重要なベリレン-3, 4, 9, 10-テトラカルボン酸ジイミドの製造法に関するものである。

(従来の技術)

ベリレン-3, 4, 9, 10-テトラカルボン酸ジイミドはアセナフテン系建築染料の重要な製造原料の一つとして古くから知られており、最近では、光学系有機材料の製造原料としても注目されている。その製造方法は、1,8-ナフタリイミドをアルカリ溶融反応によりカップリング(縮合)させた後、酸化することにより製造されていた(BIOS FINAL REPORT Nr. 1487, 21, D.R.P. 762357, 276956; F r d l., 12, 492, 493, 工業化学雑誌 54, 479 (1951), 特開昭59-205, 376 G号公報)。また、カップリング反応と酸化反応を同時に一段で行わせる方法も報告されている(Eur. Pat. 54, 806)。

(発明が解決しようとする課題)

しかしながら、従来の技術では、1,8-ナフタル

イミドに対してアルカリを大過剰使用しているにも係わらず、溶融反応において反応形態が極めて高い粘性スラリーとなることから特殊の反応器が必要で、また反応器の劣化も早いなどの問題がある。更に、アルカリ溶融による縮合反応生成物を分離する際に反応生成物が高粘性物であることから、高濃度のアルカリ溶液に高温下で水を添加しなければならず、製造上安全面に問題がある。また、分離された大過剰のアルカリは廃液として処理されている等の問題もある。

そこで、本発明者等は上記の問題点を解決すべく鋭意研究を行った結果、1,8-ナフタリイミドを高沸点溶剤中に分散させてアルカリ金属水酸化物により縮合反応させ、かつ酸化してペリレン-3,4,9,10-テトラカルボン酸ジイミドを製造することができることを見出した。また、高沸点溶剤とアルカリ金属水酸化物は回収され、再利用が可能であることを見出した。

本発明の目的は、1,8-ナフタリイミドから収率良く、かつ経済的に安価に、そして製造上の操作

の安全性が高く、反応の連続化も比較的容易となるペリレン-3,4,9,10-カルボン酸ジイミドの製造方法を提供することにある。

〔課題を解決するための手段〕

すなわち、本発明は、1,8-ナフタリイミドとアルカリ金属水酸化物に高沸点溶剤を加えて反応形態を比較的低粘性のスラリーとした状態で、縮合反応が起こる温度に加熱して縮合し、更に酸化することによりペリレン-3,4,9,10-テトラカルボン酸ジイミドを製造する方法である。

以下、本発明を詳細に説明する。

本発明で使用する高沸点溶剤としては、反応条件下で液相を示し、好ましくは沸点が200～400℃の範囲に入り、縮合反応を妨げるような酸性物質でないものであれば格別の制限はないが、アルカリ金属水酸化物に対して加熱条件下で安定である必要がある。このような高沸点溶剤としては、コールタール又は石油から分離される油や、非プロトン性極性溶剤が好ましいものとして挙げられる。例えば、コールタールから分離される油

としては、熱安定性の優れるキノリン、キナリジン、イソキノリン等の含窒素芳香族化合物又はこれらを含むタール塩基油があり、その他メチルナフタレン又はこれを含む留分も熱安定性が良く好ましい。そして、石油から分離される油としては、特に灯油と軽油が優れる。なお、当然のことであるが、これらの分離される油の主な成分を構成する化合物単独からなる油であってもよい。更に、プロトン供与性のない非プロトン性高沸点極性溶剤としては、高温下でのアルカリ金属水酸化物に対して熱安定性の良い1,3-ジメチル-2-イミダゾリジソンが好ましい。なお、これらの溶剤はあらかじめ、フェノール等の反応に支障をきたす物質、熱安定性の悪い物質等の不純物を除く処理を行っておくことが望ましい。高沸点溶剤はアルカリ金属水酸化物等の原料を溶かさなくても差し支えなく、全体が高沸点溶剤に分散した状態になって、スラリー状となればよい。

高沸点溶剤の使用量は、1,8-ナフタリイミドに対して2～10重量倍がよい。溶剤の使用量を必

要以上に大過剰にすると反応時間が長くなったり、副生成物が多くなり生成物の純度を下げることになる。溶剤の使用量が少ないと反応混合物がスラリー化せず、粘度が十分に低下しない。

本発明で使用するアルカリ金属水酸化物は、水酸化カリウム、水酸化ナトリウムが好ましく、特に水酸化カリウムが好ましい。これらは固体あるいは水溶液の状態で使用され、その使用量は1,8-ナフタリイミドに対し、水酸化カリウムとして0.5～10重量部、好ましくは2～5重量部である。水酸化アルカリ金属水酸化物は、80%以上の濃度のものを使用するのが好ましいが、50%程度の濃度の水溶液を用い、反応器中で水を蒸発除去しながら反応しても良い。

本反応は、前述した反応原料混合物を加熱して行うが、その温度は180～300℃である。温度が180℃未満であると1,8-ナフタリイミドの転化率が下がる。本反応の反応時間は、高沸点溶剤の量とアルカリ金属水酸化物の量並びに反応温度に関係するが、通常0.5～24時間である。

縮合反応終了後又は縮合反応と同時に、縮合反応生成物を酸化して、ペリレン-3,4,9,10-テトラカルボン酸ジイミドとする。すなわち、縮合反応終了後、固液分離を行いペリレン-3,4,9,10-テトラカルボン酸ジイミドのリュウコ体を単離し、水に分散させた状態で空気を吹き込むなどする公知の方法により酸化し、酸化生成物をろ取して水、有機溶剤等で洗浄した後、乾燥してペリレン-3,4,9,10-テトラカルボン酸ジイミドを得るような方法あるいは縮合反応に引き続き、空気酸化、ろ過分離して生成物を水、有機溶剤で洗浄した後、乾燥してペリレン-3,4,9,10-テトラカルボン酸ジイミドを得るような方法である。後者の方法をとれば、反応混合物を格別分離することなく、一段で縮合と酸化が行えることになる。この場合、縮合反応終了後酸化を行うこともできるし、同時にすることも可能である。その他、縮合反応終了後に酸化を行う別法として、ろ過前に水を添加してアルカリ金属水酸化物を水溶液とした後、ろ過する方法がある。

てに加熱して10時間攪拌した。温度を60℃に下げてもろ過を行い、大量の水で洗浄してペリレン-3,4,9,10-テトラカルボン酸ジイミドのリュウコ体をろ取した後、水に分散させた状態で空気酸化するという公知の方法で酸化し、酸化生成物を固液分離して水洗浄、メタノール洗浄を行い、乾燥してペリレン-3,4,9,10-テトラカルボン酸ジイミド19.0gを得た。

#### 実施例2

メチルナフタレン留分120gに86%水酸化カリウム60gと1,8-ナフタルイミド20gを加えて230℃に加熱して10時間攪拌した。温度を80℃に下げた後、水を60g加えて30分間煮沸し、ろ過して水洗浄を行ってペリレン-3,4,9,10-テトラカルボン酸ジイミドのリュウコ体を得た。ろ液から水酸化カリウムを水溶液とメチルナフタレン留分を分離回収した。リュウコ体はメタノール洗浄後、公知の方法で空気酸化を行い、酸化生成物を固液分離して水洗浄した。乾燥してペリレン-3,4,9,10-テトラカルボン酸ジイミド18.

ろ過で得られるろ液から容易に高沸点溶剤は回収され、必要に応じて蒸留精製後、再使用することができる。また、アルカリ金属水酸化物は水溶液として回収可能であり、この場合、ろ過あるいは洗浄の際に用いられる水の量を制御することにより、高濃度水溶液として回収することも可能である。回収されたアルカリ金属水酸化物の水溶液は必要により濃縮され再使用される。酸化に使用する酸化剤としては、酸素含有ガス、好ましくは空気をを用いて行うことができる。

#### 〔実施例〕

次に、実施例により本発明を説明する。なお、実施例において、%は重量%を表す。

#### 実施例1

コールタールから分離されたメチルナフタレン留分(α-メチルナフタレン44.2%、β-メチルナフタレン22.9%、ジメチルナフタレン26.1%、キノリン2.3%、アセナフテン2.3%、フルオレン2.2%)120gに、86%水酸化カリウム水溶液60gと1,8-ナフタルイミド20gを加えて、230

8gを得た。

#### 実施例3

メチルナフタレン留分120gに86%水酸化カリウム60gと1,8-ナフタルイミド20gを加えて220℃に加熱した反応混合物に、空気吹き込み管より毎時140ml割合で空気を吹き込みながら220℃で10時間、攪拌を行った。温度を80℃に下げた後、水を60g加えて30分間煮沸し、ろ過してろ液から水酸化カリウム水溶液とメチルナフタレンを分離回収した。ろ過物は水洗浄、メタノール洗浄して乾燥を行い、ペリレン-3,4,9,10-テトラカルボン酸ジイミド18.6gを得た。

#### 実施例4

キノリン80gに86%水酸化カリウム60gと1,8-ナフタルイミド20gを加えて210℃に加熱して12時間攪拌した。温度を60℃に下げた後、ろ過してキノリンを分離回収した。ろ過物を水洗浄、メタノール洗浄してペリレン-3,4,9,10-テトラカルボン酸ジイミドのリュウコ体を得た。これを、公知の方法で酸化してペリレン-3,4,9,10-

テトラカルボン酸ジイミド18.3gを得た。

#### 実施例5

1,3-ジメチル-2-イミダゾリジノン80gに86%水酸化カリウム60gと1,8-ナフタルイミド20gを加えて225℃に加熱して6時間攪拌した。室温に戻した後、ろ過してろ液から1,3-ジメチル-2-イミダゾリジノンを回収した。ろ過物を大量の水で洗浄してペリレン-3,4,9,10-テトラカルボン酸ジイミドのリューコ体を得た。これを、公知の方法で酸化してペリレン-3,4,9,10-テトラカルボン酸ジイミド18.8gを得た。

#### 実施例6

1,3-ジメチル-2-イミダゾリジノン320gに86%水酸化カリウム120gと1,8-ナフタルイミド40gを加えて225℃に加熱して6時間攪拌した。温度を170℃に下げた後、空気吹き込み管より毎時100ml割合で空気を吹き込んで6時間攪拌して酸化させた。室温に戻した後、ろ過して1,3-ジメチル-2-イミダゾリジノンを分離回収した。ろ過物を水洗浄して乾燥を行ってペリレン

-3,4,9,10-テトラカルボン酸ジイミド37.8gを得た。

#### 実施例7

1,3-ジメチル-2-イミダゾリジノン320gに86%水酸化カリウム240gと1,8-ナフタルイミド80gを加えて225℃に加熱した。温度を保持しながら空気を毎時100mlの割合で6時間吹き込み攪拌した。室温に戻した後、ろ過して1,3-ジメチル-2-イミダゾリジノンを分離回収した。ろ過物に水240gに加えて煮沸しながら30分間攪拌した。再びろ過してろ液から水酸化カリウムを水溶液として回収した後、水洗浄して乾燥を行ってペリレン-3,4,9,10-テトラカルボン酸ジイミド75.1gを得た。

#### 実施例8

灯油60gに86%水酸化カリウム30gと1,8-ナフタルイミド10gを加えて225℃に加熱した。温度を保持しながら空気を毎時100mlの割合で6時間吹き込み攪拌した。室温に戻した後、ろ過して灯油を分離回収した。ろ過物に水30g

を加えて煮沸しながら30分間攪拌した。ろ過してろ液から水酸化カリウムを水溶液として回収すると共に、ろ過物を洗浄、乾燥してペリレン-3,4,9,10-テトラカルボン酸ジイミド9.4gを得た。

#### 〔発明の効果〕

本発明の製造方法よれば、1,8-ナフタルイミドとアルカリ金属水酸化物を高沸点溶剤の存在下で、縮合反応させることで、染料料および電子材料等の製造中間体として使用されるペリレン-3,4,9,10-テトラカルボン酸ジイミドを経済的に製造することができるだけでなく、製造上の操作面も安全となる。

特許出願人

新日鐵化学株式会社

代理人

弁理士 成 瀬 勝 夫

(外3名)